THE REACTION OF CALCIUM CARBIDE AND FERRIC OXIDE

BY

ISADORE FINKELSTEIN

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMISTRY

COLLEGE OF LIBERAL ARTS AND SCIENCES

UNIVERSITY OF ILLINOIS

1922

UNIVERSITY OF ILLINOIS

----May 31,----192**2**--

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Isadore Finkelstein

ENTITLED_____THE REACTION OF CALCIUM CARBIDE AND FERRIC OXIDE

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF ____BACHELOR OF SCIENCE

_____in CHEMISTRY

_____W. S. Putnam_____

Instructor in Charge

APPROVED: J. C. Parr

ACTING HEAD OF DEPARTMENT OF CHEMISTRY

UNIVERSITY OF ILLINOIS

May 31, 192

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Isadore Finkelstein

ENTITLED ____ THE REACTION OF DALGIN, CHONDRUS AND FERRIC OXIDE

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF ____ BACHELOR OF SCIENCE

IN CHEMISTRY

Instructor in Charge

APPROVED: HEAD OF DEPARTMENT OF CHEMISTRY

ACKNOWLEDGMENT

TABLE OF CONTENTS

TABLE OF CONTENTS

INTRODUCTION

This work was done in connection with that of W. J.
Farrel on the Desulphurization of steel by calcium carbide.
The purpose of the work to be described was to determine
whether or not calcium carbide will react as a reducing agent
in case oxides were present in the steel and to what degree
the reduction is carried out. S. Cohen has done work on the
reaction of calcium carbide and ferrous sulfide. The results
of the men mentioned above along with the results obtained in
this paper may be considered as one, and thus give a compre-
hensive report on the effects of calcium carbide as a desul-
phurizing and deoxidizing agent. The great need in the steel
industry, is a method to eliminate sulphur and phosphorus
from steel without the electric furnace temperatures. The
conditions of the investigation do not duplicate those of the
open hearth furnace, but it was undertaken with the hope of
learning something more than is known about the chemical
activity of CaC_2 that could be applied in making steel.

HISTORICAL

Calcium Carbide was first detected by Wöhler in 1862. On heating a Ca-Zn alloy with carbon at a high temperature he obtained a hard substance with a metallic luster, which became grey on exposure to the atmosphere. The discovery of Calcium Carbide is usually accredited to Moisson, who prepared it in an electric furnace. He heated coal and calcium oxide at temperatures up to about 2000 degrees C and obtained the carbide. The carbide is formed according to the equation given below:

$$CaO + 3C = CaC_2 + CO$$
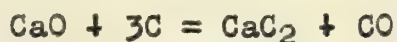
The present day manufacture of Calcium Carbide is according to the equaltion given above. The carbon is in the form of finely powdered coal. Care is taken that the coal is of low sulphur content. This is necessary in order to prevent formation of hydrogen sulfide when the carbide is used for the preparation of acetylene gas. The first and largest use for the carbide is in the production of acetylene.

$$CaC_2 + H_2O = C_2H_2 + Ca(OH)_2$$
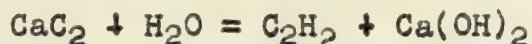
Calcium carbide according to Erlwein, (1) Wrath and Bentner will decompose very slowly. These men did extensive work on the decomposition of the carbide by heat. Their results show that when CaC_2 is heated to 1000° C slow decomposition takes place. They did not identify the product formed, but assumed it to be a subcarbide of calcium. No metallic

calcium could be detected. On treatment with water no acety-
lene was evolved, but when nitrogen was passed over the
material the compound $CaCN_2$ was formed. They showed that after
heating CaC_2 for 10 hours at $1000^{\circ}C$ the carbide analyzed
36.6% CaC_2 whereas the sample to start with was 72% CaC_2. They
also noted that NaCl, CaCl and iron powder aided in the de-
composition of the carbide. When CO gas is passed over CaC_2
at temperatures between $200-250^{\circ}C$, there is a reaction taking
place as indicated

$$CaC_2 + CO = CaO + 3C$$
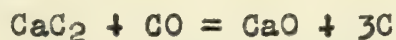
At $1600^{\circ}C$ this reaction is reversible. It may be well
to note here that according to this equation the carbide must
be formed at high temperatures.

Since my problem is one of a reducing nature, it may
be well to summarize the work that has been done along this
line. As early as 1899 we find Tarugi (2) worked on the re-
ducing properties of calcium carbide. He reduced copper
oxide at bright red heat and the chloride of copper at about
$400^{\circ}C$. Kügelgen (3) has done extensive work on the reducing
properties of calcium carbide. He worked with the oxides of
Pb, Cu, Ag, Zn, Hg, Sn, As, W, Mn, Fe, Ni, Al.

If a mixture as indicated by the equation below is
heated to dull red heat a reduction takes place as indicated:

(1) $PbO + CaC_2 = Pb + CaO + 2C$
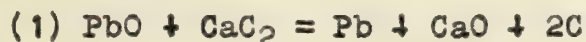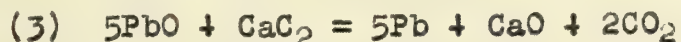
At dull red heat the carbon, which is the graphitic
form will react as indicated:

(2) $4PbO + 2C = 4Pb + 2CO_2$
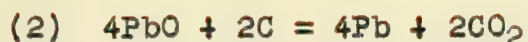
If the charge contains an excess of oxide it will re-act according to equation (3)

(3) $5PbO + CaC_2 = 5Pb + CaO + 2CO_2$

This reaction will take place at higher temperatures, while 1 and 2 at lower temperatures. The chloride of Lead reacts in a similar manner.

(4) $PbCl_2 + CaC_2 = Pb + CaCl_2 + 2C$
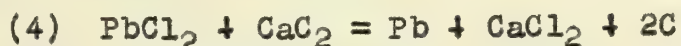
A mixture of the oxide and chloride react according to (5)

(5) $4PbO + PbCl_2 + CaC_2 = 5Pb + CaCl_2 + 2CO_2$
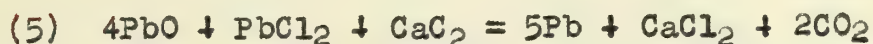
These reactions may be considered as the general re-actions of calcium carbide with oxide and chlorides of all of the metals named previously.

Fröhlich (4) showed that 1/10 to 1/4 ton of CaC_2 was necessary to produce 1 ton of copper. Kügelgen worked with the oxides of iron and CaC_2. He was able to get a reduction, but claims that it is of no definite value as in the case of lead and copper. From what has been discussed so far we can represent the reduction of oxides by carbides by two general equations:

(1) $3MO + CaC_2 = CaO + 3M + 2CO$

(2) $5MO + CaC_2 = CaO + 5M + 2CO_2$
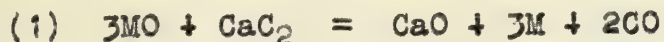
The first takes place with oxides difficultly reduced (according to Newmann and Fröhlich). The second with oxides easily reduced (Kügelgen).
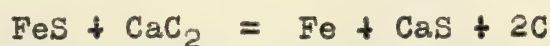
Calcium carbide has been used as a desulphurizing and deoxidizing agent in the metallurgical industry mainly in the electric furnace where high temperatures are possible. T. M. Camp and C. B. Francis in their book, "The Making Shaping and Treating of Steel" give the following theory in regards to the action and formation of Calcium Carbide in the Heroult Furnace. Under the influence of the high temperatures that exist around the electrode the CaO and carbon in their vicinity combine to form calcium carbide. The authors maintain that it is at that point when desulphurization takes place. The slags of the Heroult furnace contain various amounts of free CaC_2. The authors claim that a considerable quantity of CaC_2 in the slag is a guarantee that the bath is deoxidized.

$$CaC_2 + \begin{matrix} 3FeO \\ 3MnO \end{matrix} = \begin{matrix} 3Fe \\ 3Mn \end{matrix} + CaO + 2CO$$
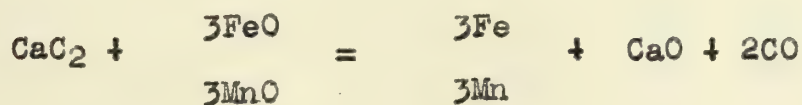
Moisson (5) did work on the reaction of sulfides with calcium carbide.

$$FeS + CaC_2 = Fe + CaS + 2C$$

From the above reactions one can see that CaC_2 in the slag serves as a deoxidizer and desulphurizer.

EXPERIMENTAL

For my experimental work it was necessary to determine accurately, the purity of the calcium carbide and iron oxide used. The iron oxide was determined by the Permanganate method. The CaC_2 was analyzed by two methods.

(1) Absorbtion in suprous chloride.

(2) Difference in weight method.

These methods can be combined so that one is a check for the other. The apparatus illustrated below was used.
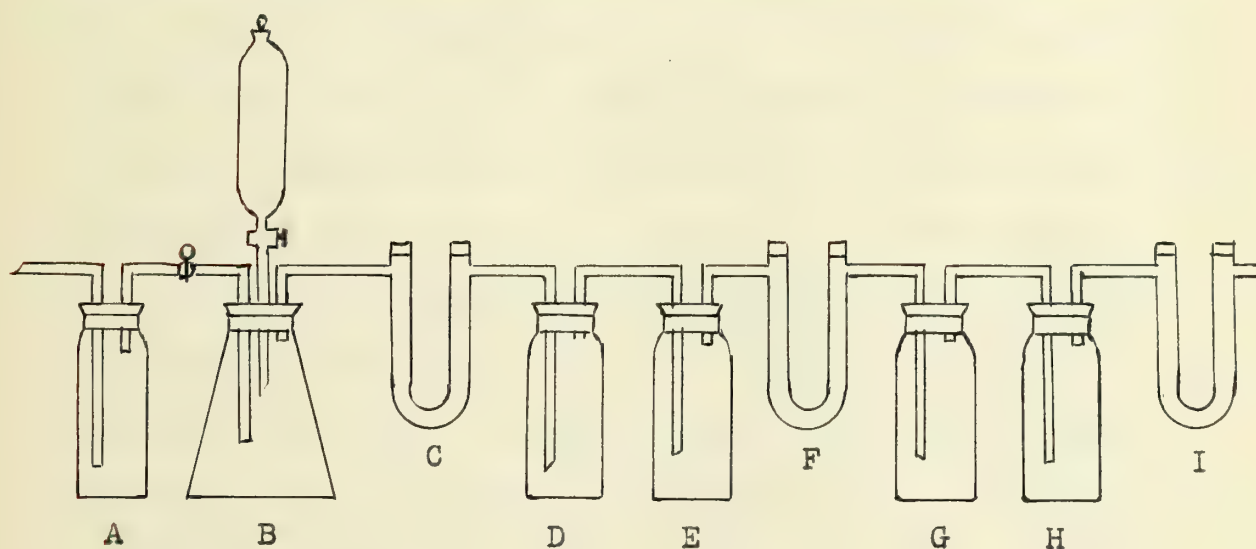
A contains H_2SO_4 to dry air passing through apparatus.

B is the acetylene generator.

C a calcium chloride tube.

D a trap

E contains a hypochlorite colution for removing sulfur and phosphorus.

F a calcium chloride tube.

G and H contain an ammoniacle solution of cuprous chloride.

I is a $CaCl_2$ tube.

The cuprous chloride solution was prepared as given in Bloxam.

30 grams of black copper oxide dissolved in 200 c.c. of HCl and boiled for 30 minutes with 24 grams of finely divided copper. The brown solution is poured into 1750 c.c. of $H2O$, allowed to settle, the water drawn off by a siphon and the precipitate rinsed into a 1/2 liter bottle. This is filled with water and when the ppt. is settled the water is drawn off as before. 120 grams of NH_4Cl are added and the bottle filled with water and shaken. For precipitation this solution is poured into 1/10 its bulk of strong ammonia.

A weighed sample of Calcium Carbide is placed in the dry flask B which is fitted with a dropping funnel and delivery tubes as indicated. A slight excess over the calculated amount of water is added. It is best to use a 20% salt (NaCl) solution as this will reduce the heating effect. B and C are carefully weighed (to the third place), G, H and I are also weighed. The apparatus is connected to tightly fitting rubber tubing. Stop cock o is opened slightly to allow a slow stream of dry air to pass through the apparatus. The water or salt solution is then allowed to drop very slowly. This is necessary or else the gas will pass out unabsorbed. After the reaction has stopped, the current of air is allowed to

pass through for about 2 hours in order to make sure that all of the acetylene has passed into G and H. B and C and G, H and I are again weighed. Since, according to the two equations,

(1) $CaC_2 + H_2O = Ca(OH)_2 + C_2H_2$

(2) $C_2H_2 + CuCl + 2NH_3 = Cu\,C\,C\,Cu + 2NH_4Cl$
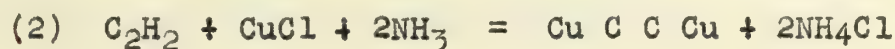
all of the products remain in the apparatus, the loss in weight of B and C should equal the gain in weight of G, H and I. The loss in weight of B and C equals the weight of C_2H_2 produced, corrected for weight of hydrogen sulfide and phosphide evolved. The cuprous acetylide comes down as a red precipitate which is insoluble in water. In the analysis, the absorption method was omitted. The difference method is fairly accurate as will be seen by the results obtained.

| WEIGHT OF CaC$_2$	WEIGHT OF APPARATUS B+C before	WEIGHT OF B + C after	DIFFERENCE = Wt. of C$_2$H$_2$	%PURE CaC$_2$	AVERAGE
23.4837	372.697	368.450	4.247	44.57	
7.0663	379.011	377.715	1.296	44.60	
7.6758	304.470	302.987	1.483	47.29	
7.7358	336.346	334.937	1.409	44.80	45.31
Second Sample					
5.3588	276.544	274.894	1.650	75.75	
4.4914	229.132	227.698	1.434	78.60	
5.1221	278.510	276.929	1.581	76.02	76.79

The first sample used was very finely divided material which had been exposed to the air. For this reason, the sample is rather low in carbide. The second sample was coarsely ground and only large lusterous lumps of carbide were ground. The iron oxide ran 88.6% and 90% pure Fe_2O_3. Only traces of S were found in either sample.

FUSIONS

In order to determine the reaction of Calcium Carbide on iron oxide various charges and temperatures were tried. The ultimate aim was to reach a temperature condition similar to that in the open hearth furnace. For temperatures up to 1250°C a gas furnace was used and above this temperature an oil furnace was used.

Fusion No. I

	A	B
CaC_2	6.150 grams	5.673 grams
Fe_2O_3	15.375 grams	14.182 grams
C	1 gram	1 gram

This charge is calculated according to the equation:

$$CaC_2 + Fe_2O_3 = 2Fe + CaO + 2CO$$
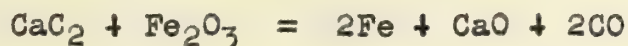
All figures are based on chemically pure materials. The two charges were heated for 3 hours at 1050 to 1100°C. In both cases the charges were slightly fused, but did not adhere to the crucibles. The fused charges were ground and treated for undecomposed CaC_2. The charge was placed in B. Water was first added, then a dilute solution of HCl, but no

acetylene was detected in the cuprous chloride solution.

Two similar charges were then heated to 1200-1250°C for three hours. At this temperature the charges were partly fused and adhered to the crucible. On cooling, the upper part of the charge contained a grey powder, which on analysis was found to be iron. In this case undecomposed carbide was analyzed for, but none was detected. The free iron in the charge could not be determined as there was present with it unreacted Fe_2O_3 and perhaps other iron compounds as well.

In the next fusions the charges were made up according to this equation.

$$5Fe_2O_3 + 3CaC_2 = 10Fe + 3CaO + 6CO_2$$
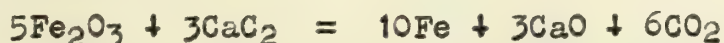
Charges	C	D	E	F
CaC_2	5.520	5.438	5.330	5.401
Fe_2O_3	25.850	25.31	25.00	25.23

12 grams of slag material of the composition given below were added to charges E and F.

$$Al_2O_3 \ - \ 3 \text{ grams}$$
$$CaCO_3 \ - \ 5 \text{ grams}$$
$$Na_2CO_3 \ - \ 5 \text{ grams}$$
$$CaF \ - \ 5 \text{ grams}$$
$$SiO_2 \ - \ 12 \text{ grams}$$

These charges were heated to white heat, approximately 1400°C, for two hours. No attempt was made to pour these charges. When removed from the furnace the charges were fluid. A glass like slag was produced in all four charges.

Charge C contained a small bead of iron at the bottom weighing .2068 grams. Charge E contained a bead weighing 1.253 grams. No carbide was detected on analysis. From the above results it showed that most of the Fe_2O_3 went into the slag. The addition of slag material produced a larger button. If we assume 1.253 grams, the weight of all the iron reduced in charge E, then only 1.789 grams of Fe_2O_3 was reduced by the carbide. This is a reduction of 7.15%

The next charges contained the calculated amount of Fe_2O_3 plus an excess approximately equivalent to the amount that went into the slag in charges C, D, E and F. The new charges were given the same heating and then poured in an iron mold. Graphite crucibles were used here instead of the clay crucibles.

RESULTS

Charges	G	H	I
CaC_2 used	6.27	6.4	7.27
Fe_2O_3 used	50	50	60
Wt. of Fe	14.34	26.76	21.03
% Reduction	28.7	53.5	35.00

The above table gives the results obtained in the last fusion. The slag in each case could be partly poured. In no case was the iron button larger than about 4 grams. The slag contained much of the free iron in the form of small beads. The slag was broken up to remove the beads of iron. A strong magnet was used to separate the iron from the slag.

This was added to the iron buttons. Under the conditions of the charge and the temperature to which it was heated it is not probable that any of the iron that was removed by the magnet was magnetite. Any Fe_3O_4 formed could react according to the equation below.

$$Fe_3O_4 + C = 3FeO + CO$$
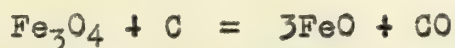
This reaction takes place at 1175°C. The temperature of the fusion was about 1400°C. From this I conclude that there was little or no magnetite formed in the charge.

Before dissolving the iron a microscopic examination was made of the iron buttons of charges H and I.
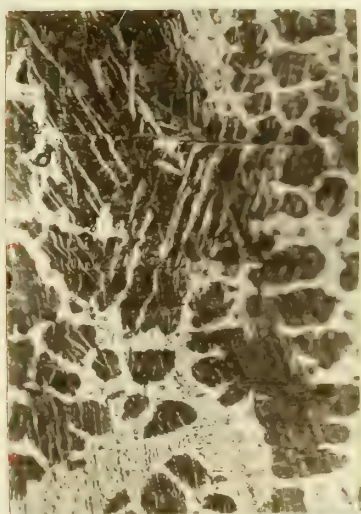
$\times$ 100 $\qquad\qquad\qquad\qquad$ $\times$ 750

The microphotographs are characteristic of medium carbon steel, approximately 45 carbon. The difference in structure is due to a change in the rate of cooling.

CONCLUSIONS

(1)   The results clearly show that when calcium carbide is heated in the presence of Fe_2O_3 at 1000° a slight reducing action takes place. The reaction increases as the temperature is increased. Note last results.

(2)   Since no acetylene could be detected when the fused charges were treated with water and dilute HCl it seems that the carbide is not present as CaC_2, but in some form undetermined.

(3)   At temperatures of 1400° and above there is a distinct reduction as shown in the data.

(4)   The iron produced is of medium carbon content. Approximately 0.45%.

(5)   The fluidity of the slag seems to have an apparant e effect on the separation of the reduced iron.

(6)   The results clearly show that when CaC_2 is added to remove sulphur from steel it also reacts as a deoxidizing agent when oxides are present. Whether or not calcium carbide is of any commercial value as a reducing agent the writer cannot say. The results indicate that there is a distinct reaction taking place at or neat temperatures maintained in an open hearth furnace.

Note: - This thesis represents one semesters work. Had more time been devoted, many more results would have been obtained and perhaps a much better understanding and explanation of the problem.

BIBLIOGRAPHY

1. Z. Elect.   -17 - 177 - 9

2. Gazetta   1899 29: 509-512

3. Z. E.   1901 -7-   541-550
                                    557-568
                                    573-580

4. Zeitssh. f. Anguvchem 1899 - 1179

5. J. O. C.   1898   All 333